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Variations in soil properties and herbicide sorption coefficients with depth in relation to PRZM (pesticide root zone model) calculations

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ABSTRACT

There are few experimental data available on how herbicide sorption coefficients change across small increments within soil profiles. Soil profiles were obtained from three landform elements in a strongly-eroded agricultural field and segmented into 2-cm intervals to 0.6 m depth in the knoll (eroded-upper slope), to 1.0 m depth in the toeslope (deposition zone) and to 1.6 m depth in the trough (eroded waterway). Soil samples were analyzed for soil organic carbon content (SOC) ($n=154$), soil pH ($n=155$), soil carbonate content ($n=126$), CEC ($n=126$), soil texture ($n=32$), bulk density ($n=160$), 2,4-D [2,4-(*dichlorophenoxy*) *acetic acid*] or glyphosate [*N-phosphonomethylglycine*] sorption by soil (Kd) ($n=90$), and 2,4-D or glyphosate sorption per unit soil organic carbon (Koc) ($n=90$). Considering all soil profiles, 2,4-D Kd values ranged from 0.12 to 2.61 L kg^{-1} and were most strongly influenced by variations in SOC. In contrast, glyphosate Kd values ranged from 19 to 547 L kg^{-1} and were predominantly controlled by variations in soil pH and clay content. Two hundred and fifty-two PRZM (pesticide root zone model) version 3.12.2 simulations were also performed. PRZM predicted that glyphosate would be immobile in soils even under an extreme rainfall scenario of 384 mm at one day after herbicide application. In contrast, for 2,4-D, PRZM predicted that up to 6% of the applied herbicide would move to a 15 cm depth under an actual rainfall scenario. PRZM output was particularly sensitive to input values of Kd, relative to input values of soil properties. The greatest change to PRZM outputs occurred when Kd values of toeslope profiles, ranging from 0.16 to 1.77 L kg^{-1}, were replaced by those measured in knoll profiles, ranging from 0.12 to 0.50 L kg^{-1}, when the amount of 2,4-D leached to a 15 cm depth increased by 29,081% (from 0.09 to 26.17 g ha^{-1}) under an actual rainfall scenario. We conclude that, when pesticide fate models such as PRZM are being used in policy analyses at larger-scales, data on Kd values in different landform elements and at the soil horizon level could be important for strengthening pesticide leaching predictions.

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1. Introduction

Herbicide fate models can be used to estimate herbicide transport by volatilization, leaching, runoff and water-eroded soil. When using these models, soil profiles are divided into layers to optimize computations and numerical accuracies (Jarvis and Larsson, 1998). For example, for the pesticide fate model PRZM (pesticide root zone model), pesticide volatilization and runoff can be better estimated if the first 10 cm of the soil profile is divided into 0.1 mm thick layers, while the remaining soil profile is to be divided into 1 to 30 cm layers (Carsel et al., 1998). Herbicide sorption coefficients (measures of herbicide sorption by soil) are among the most sensitive input parameters in herbicide fate models (Boesten and van der Linden, 1991; Dubus et al., 2003). However, there are few experimental data available on how herbicide sorption coefficients change across small increments within soil profiles (Symko and Farenhorst, 2008).

In calcareous prairie landscapes that have been subjected to intensive tillage practices for several decades, soil profiles in upper-slopes (i.e., convex elements [knolls]) are usually low in soil organic carbon content (SOC), but high in soil carbonate content ($CaCO_3$) and soil pH, relative to soil profiles in lower-slopes (i.e., concave elements, e.g. [toeslopes]) (Papiernik et al., 2007). Since these soil characteristics can affect herbicide sorption, we hypothesize that soil profiles in upper-slopes will have distinct herbicide sorption coefficients from soil profiles in lower-slopes.

Two herbicides were selected, glyphosate and 2,4-D. Glyphosate is a nonselective herbicide that is widely used in North America particularly since the expansion of the cultivation of glyphosate tolerant crops. Glyphosate is very strongly sorbed by soil but sorption decreases with increasing soil pH (Sprankle et al., 1975; De Jonge et al.,

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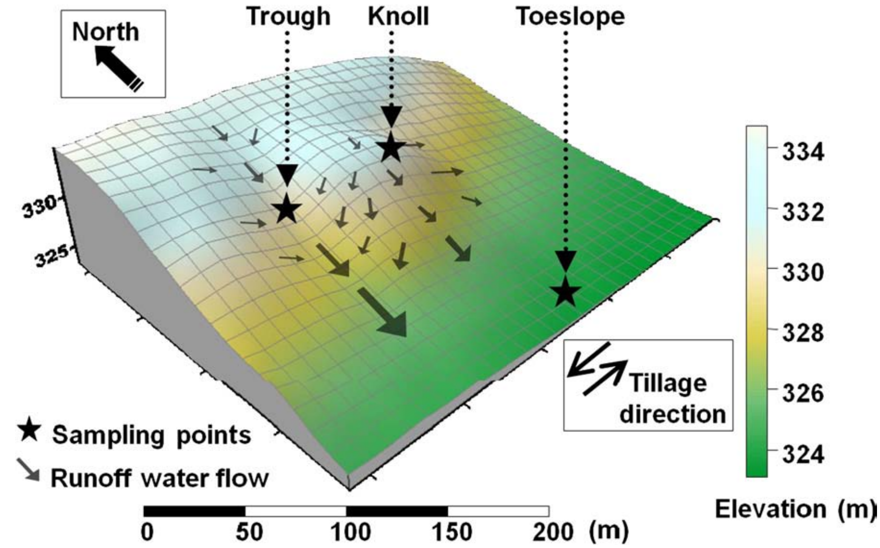

Fig. 1. Locations of sampling points in knoll (eroded-upper slope), trough (eroded water-way), and toeslope (deposition zone) landform elements.

2001). The herbicide 2,4-D is widely used to control broadleaf weeds, including glyphosate tolerant canola volunteers. 2,4-D is weakly sorbed by soil particularly in alkaline soils that are low in SOC (Calvet, 1989; Senesi, 1992).

The objectives of this study were to determine how soil properties and herbicide sorption coefficients vary in and between soil profiles of a heavily-tilled calcareous prairie landscape, and the effect that these variations have on estimating herbicide leaching using PRZM.

2. Material and methods

2.1. Chemical

The 2,4-D stock solution was analytical-grade (95% chemical purity; Sigma-Aldrich Co., St. Louis, MO) together with [U-*phenyl*-^{14}C] (99% radiochemical purity; specific activity 9.25 MBq mmol^{-1}; Sigma-Aldrich Co., St. Louis, MO) 2,4-D. The glyphosate stock solution was analytical-grade (99% purity; Chem Service, West Chester, PA) together with [*phosphonomethyl*-^{14}C] (95% purity; specific activity 89 MBq mmol^{-1}; Sigma-Aldrich Co., St. Louis, MO) glyphosate.

2.2. Study site and soil profiles

Seven soil profiles were collected within a 1-m radius in each of three landform elements (knoll, trough, toeslope: Fig. 1) in an agricultural field near Morris, MN, United States. The soil profiles were collected to 0.6 m depth in the knoll (eroded-upper slope), to 1.0 m depth in the toeslope (deposition zone) and to 1.6 m depth in the trough (eroded water-way), using 3-inch (7.6-cm) Giddings hydraulic probes. The depth of sampling varied among the landform elements such that part of the C-horizon was included in each soil profile (Table 1). Soil profiles in the knoll were classified as a fine-loamy, mixed, superactive, frigid Typic Eutrudepts (Langhei series), those in the trough as fine-loamy, mixed, superactive, frigid Pachic Argiudolls (Aastad series), and those in the toeslope as fine-silty, mixed, superactive, frigid Calcic Hapludolls (Brandt series) (Soil Survey Staff, 2008).

The agricultural field is characterized by undulating topography with slopes <11%. It has been moldboard plowed on an annual basis for at least 40 years. Tillage erosion was the largest contributor to soil loss in the knoll (Li et al., 2008). The trough and toeslope profiles showed evidence of soil accumulation, receiving tillage-translocated soil from nearby convex elements (Li et al., 2008). Water-induced soil loss was greater in the trough where water converges, than on the knoll where water diverges (Li et al., 2008).

2.3. Soil properties and herbicide sorption

Each core was sectioned into 2-cm segments. For each of the three landform elements, the 7 segments from the same depth were combined and then air-dried and sieved (2-mm screen). This yielded 30 samples in the knoll, 80 samples in the trough and 50 samples in the toeslope. The bulk density of each sample was measured by weight (without stones) as described in Li et al. (2008). Soil properties were determined as follows, whereby the number of samples used for each soil analysis varied according to available resources such as student time, and the expected importance of the soil characteristic to explaining variations in herbicide sorption with depth. Soil organic carbon content ($n=154$ whereby $n=28$ for knoll, $n=77$ for trough, and $n=49$ for toeslope) was determined by dry combustion of 0.12 g oven-dried soil using a Leco model CHN 600 C and N determinator after removing inorganic carbon by digestion with 6 M HCl (Nelson and Sommers, 1982). Soil pH ($n=155$ whereby $n=29$ for knoll,

Table 1
Scenarios used in PRZM simulations to assign Kd values to layers in knoll, toeslope and trough profiles.

Scenario	Knoll	Toeslope	Trough
	Kd values [L kg^{-1}]		
L1: measured values based on soil cores sectioned into 2-cm segments	Ranging from 0.12 to 0.50	Ranging from 0.16 to 1.77	Ranging from 0.21 to 2.61
L2: average value across soil profile	0.28	1.06	0.86
L3: average value of A-horizon (0–16 cm)	0.44	1.64	1.57
L4: average values for each soil horizon	Ap (0–16 cm) = 0.44	Ap (0–16 cm) = 1.64	Ap (0–16 cm) = 1.57
	AC (16–24 cm) = 0.37	A (16–26 cm) = 1.71	A (16–46 cm) = 1.52
	C1 (24–60 cm) = 0.19	Bw (26–84 cm) = 1.04	Bt (46–144 cm) = 0.62
		C (84–100 cm) = 0.18	C (144–160 cm) = 0.33

$n=76$ for trough, and $n=50$ for toeslope) was measured using 20 ml of 0.01 M $CaCl_2$ and 10 g air-dried soil (McKeague, 1978). Total carbonate content ($n=126$ whereby $n=29$ for knoll, $n=47$ for trough, and $n=50$ for toeslope) was determined using a volumetric calcimeter that measures evolved carbon dioxide upon addition of 6 M $HCl \cdot FeCl_2$ to a soil sample (Loeppert and Suarez, 1996). Soil texture ($n=32$ whereby $n=6$ for knoll, $n=16$ for trough, and $n=10$ for toeslope) was measured using the hydrometer method (Gee and Bauder, 1986). The cation exchange capacity (CEC) ($n=26$ whereby $n=6$ for knoll, $n=10$ for trough, and $n=10$ for toeslope) was determined at pH 7 with ammonium acetate (Chapman, 1965).

Herbicide sorption by soil ($n=90$ whereby $n=19$ for knoll, $n=35$ for trough, and $n=36$ for toeslope) was assessed for each herbicide using batch equilibrium experiments. The 2,4-D or glyphosate solutions were prepared in 0.01 M $CaCl_2$ by combining cold and radiolabeled herbicide, the concentration being 1 mg L^{-1} with a radioactivity of 16.7×10^{-3} Bq L^{-1}. The 2,4-D or glyphosate solutions (10 ml) were added to soil (5 g) in Teflon tubes (in duplicate) and rotated at 60 rpm (Rotamix, Appropriate Technical Resources Inc., Laurel, MD) for 24 h to establish equilibrium. Samples were then centrifuged at 7550× *g* for 10 min. Aliquots (1 ml) of supernatant (in duplicate) were removed from each tube and used to determine the amount of 2,4-D or glyphosate remaining in solution. The amount of radioactivity in herbicide solutions and samples from experiments was determined using Liquid Scintillation Counting (LSC) with automated quench correction (#H method) (LS 7500 Beckman Instruments, Fullerton, CA). Radioactivity was measured using 10 mL of Scintisafe scintillation cocktail (Fisher Scientific, Fairlawn, NJ) and a maximum counting time of 10 min.

The 2,4-D or glyphosate sorption coefficient, Kd [L kg^{-1}] was calculated by Kd = Cs / Ce where Cs = the amount of herbicide sorbed by the soil [g kg^{-1}] and Ce = the herbicide concentration of the soil solution at equilibrium [g L^{-1}]. The amount of 2,4-D or glyphosate sorption per unit soil organic carbon, Koc, was also determined: Koc = (Kd / SOC) × 100.

Curve fitting was performed using Sigma Plot version 6 (1986–2000, SPSS Inc.) to determine appropriate models between independent (SOC, soil pH, total soil carbonates, CEC, clay) and dependent (Kd or Koc) variables.

2.4. Risk of herbicide leaching

Two hundred and fifty-two PRZM version 3.12.2 simulations were performed: 18 simulations for the herbicide glyphosate and 234 simulations for the herbicide 2,4-D. We selected PRZM version 3.12.2 because this pesticide fate model is being used as a policy tool in assessments of the risk of herbicide movement by leaching, runoff and water-eroded soil on agricultural land across Canada (McQueen et al., 2007). PRZM is also being used in pesticide registration and evaluation by the Pesticide Management Regulatory Agency, Health Canada. For the simulations, either 2,4-D (445 g ha^{-1}) or glyphosate (825 g ha^{-1}) was applied on May 1, 2004 at approximate recommended field rates. Calculated parameters were the total amount of 2,4-D or glyphosate moved to 15, 45, 60, 100 or 160 cm depth between May 1 and September 31, 2004. In agreement with the depth to which soil samples were collected in the field, the simulations used a maximum depth of 60, 100 and 160 cm for the knoll, toeslope and trough profiles, respectively.

The simulations utilized a daily time step (24-h) and were grouped as follows. *I. Base case (2 herbicides × 6 rainstorm scenarios × 3 soil profiles = 36 simulations)*: Herbicide leaching was calculated in each soil profile whereby input parameters on soil properties (i.e., soil organic carbon content, bulk density, %sand, and %clay) and herbicide sorption parameters (i.e., glyphosate Kd or 2,4-D Kd) where derived from our measurements. This was done for each of six chosen rainstorms on May 2, 2004 and then resuming actual rainfall data until

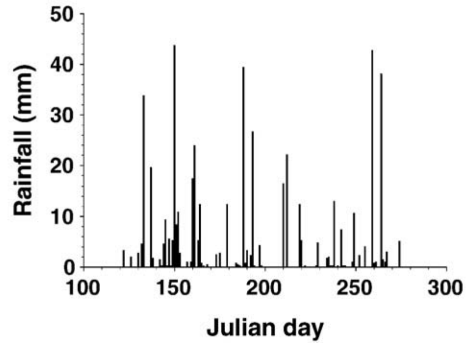

Fig. 2. Rainfall data from May 1, 2004 (Julian day 122) to September 30, 2004 (Julian day 274) obtained from a national weather station in Morris, Minnesota (National Climatic Data Center, 2007), located a few kilometers from the research site.

September 30, 2004 (Fig. 2). The six chosen rainstorm scenarios on May 2, 2004 were: (R1) a 0 mm rainfall, which was equivalent to that reported for Morris on May 2, 2004 (National Climatic Data Center, 2007); (R2) a 28.4 mm rainfall, (R3) a 51.6 mm rainfall, (R4) a 86.9 mm rainfall, and (R5) a 141.5 mm rainfall, which have in west central MN a 24-h return period of 2-months, 1-year, 10-years and 100-years, respectively (Huff and Angel, 1992); and (R6) a 384 mm rainfall, which is the largest 24-h rainfall ever recorded by the official National Weather Service (on August 17, 2007) for a location in MN (Climatology Working Group, 2007). In all rainfall scenarios, there was also a small rainfall (3.3 mm) on May 1, 2004.

II. Case study one (1 herbicide × 6 rainstorm scenarios × 2 soil profiles × 12 replacement scenarios = 144 simulations): The differences in 2,4-D leaching observed between soil profiles were further examined in a sensitivity analyses. Specifically, one or more soil properties or herbicide coefficients measured in the knoll profile were replaced by those measured in the toeslope profile. Likewise, one or more soil properties or herbicide coefficients measured in the toeslope profile were replaced by those measured in the knoll profile. In total, 12 replacement scenarios were considered in each soil profile under each of the six rainfall scenarios. *III. Case study two (1 herbicide × 6 rainstorm scenarios × 3 soil profiles × profile segment scenarios = 72 simulations):* The sensitivity of PRZM to 2,4-D Kd was investigated for each profile. Kd values were assigned as follows: (Table 1): (L1) the values were variable with depth according to the data obtained for the 2 cm profile segments in the profile, (L2) the values were constant with depth according to the calculated average of all soil samples in the soil profile, (L3) the values were constant with depth according to the calculated average of all soil samples in the A-horizon (0–16 cm); and (L4) the values were variable with depth according to the calculated average values in soil samples of specific horizons. Again, six rainfall scenarios were considered.

In all of the above simulations, PRZM simulations were conducted as recommended (Carsel et al., 1998) such that the first 10 cm of the soil profile was divided into 0.1 mm thin layers, and the remaining soil profile was divided into 0.5 cm layers. Other model assumptions were as follows. Field capacity and wilting points were calculated as recommended in Carsel et al. (1998), using data on SOC, soil bulk density, %sand and %clay. All simulations were done starting soils at field capacity and allowing a warm-up time of three years to ensure that moisture conditions were more realistic at the time that herbicides were applied. Herbicide half-lives were set at 10 days for 2,4-D and 12 days for glyphosate (FOOTPRINT Consortium, 2006). The Henry's Law constant, used in the model to calculate herbicide volatilization, was set at 1.4×10^{-9} for 2,4-D and 6.6×10^{-19} for glyphosate (FOOTPRINT Consortium, 2006), even though PRZM predicts no volatilization until the Henry's Law constant is about 1×10^{-4}. The field size was set at 2.72 ha because this was the size of the experimental plot which we used previously to characterize herbicide sorption by surface soils (Farenhorst et al., 2008). Knoll, trough and toeslopes profiles received the same amount of water, all in the form of rain. Evapotranspiration was calculated as suggested by Hargreaves and Samani (1985). Slope gradients were set at 7% for the knoll, 5% for the trough and 2% for the toeslope. Soil profile drainage was set at well-drained for all profiles. Based on field characteristics, the soil erodibility factor, K, was set at 0.34, the crop/vegetation and management factor, C, was set at 0.55, and the support practice factor, P, was set at 1.0 (Carsel et al., 1998).

3. Results

Knoll profiles were generally more alkaline (Fig. 3A) and had greater amounts of carbonates (Fig. 3B) than toeslope and trough profiles. Knoll profiles usually had less SOC (Fig. 3C) and also smaller CEC values (Fig. 3D) than samples from toeslope and trough profiles. Samples from knoll profiles had a larger clay content (Fig. 3E) than samples from toeslope profiles and a greater sand content (Fig. 3F) than samples from trough profiles. All Ap-horizons had similar glyphosate Kd (Fig. 3G) and Koc (Fig. 3H) values but, at deeper depths,

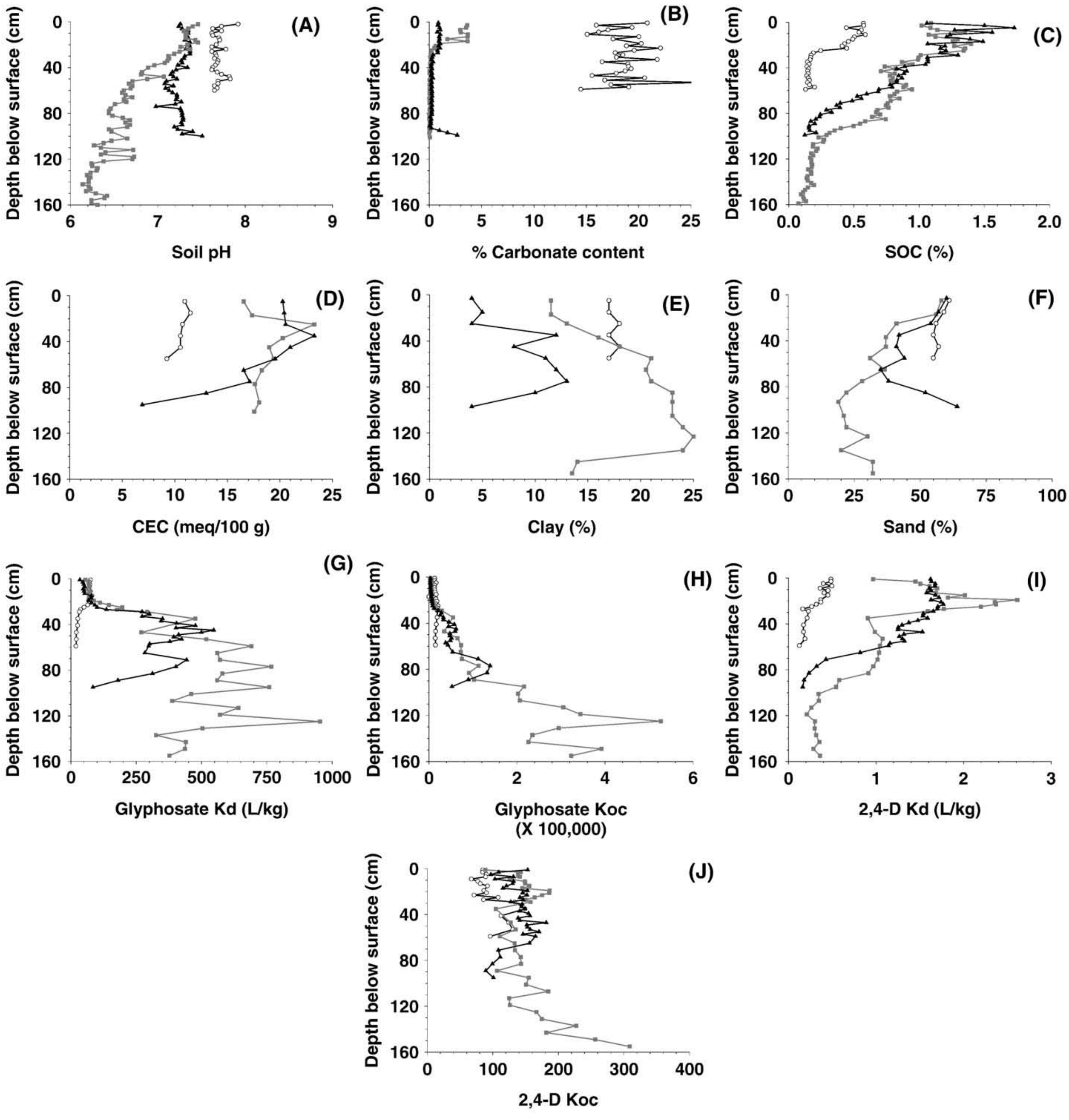

Fig. 3. Measured data on (A) soil pH, (B) soil carbonate content, (C) soil organic carbon content, (D) cation exchange capacity, (E) clay content, (F) sand content, (G) glyphosate sorption coefficient, (H) glyphosate sorption per unit soil organic carbon, (I) 2,4-D sorption coefficient, and (J) 2,4-D sorption per unit soil organic carbon in soil profiles of knoll (eroded-upper slope) (white circles), trough (eroded water-way) (grey squares), and toeslope (deposition zone) (black triangles) landform elements.

knoll profiles had generally smaller glyphosate sorption coefficients than samples from trough and toeslope profiles. Knoll profiles had generally smaller 2,4-D Kd (Fig. 3I) and Koc (Fig. 3J) values than trough and toeslope profiles. However, regardless of the soil profile, all C-horizons had particularly small 2,4-D Kd values (Fig. 3I). The 2,4-D Kd was greater in the trough profile between 10 to 20 cm depth compared to other depths in the trough profile and to 2,4-D Kd values in the knoll and toeslope profiles (Fig. 3I). The 2,4-D Koc was relatively large at depths between 150 and 160 cm in the trough profile (Fig. 3J).

Glyphosate was relatively immobile in soils because even under rainfall scenario R6 (384 mm), PRZM outputs demonstrated no glyphosate leaching to 15 cm depth (data not shown). In contrast, for 2,4-D, PRZM predicted that about 6% of the applied herbicide moved to 15 cm depth in the knoll profile for climatic conditions occurring at the site between May 1 and September 30, 2004 (Table 2). However, under this scenario, the 2,4-D loss to 45 cm depth was only 0.03% of that applied (Table 2). As expected, the amount of 2,4-D leached to depth increased with increasing rainfall intensity on May 2 (Table 2). In general, PRZM estimated significantly less 2,4-D loss in toeslope and trough profiles than in the knoll profile (Table 2). Even for rainfall with a return period of 10 years (R4), PRZM predicted no 2,4-D loss in toeslope and trough profiles at a 45 cm depth (Table 2).

When replacing the Kd values in toeslope profiles by those measured in knoll profiles, the amount of 2,4-D leached to 15 cm increased by 29,081% (from 0.09 to 26.17 g ha^{-1}) under the climatic conditions occurring at the site between May 1 and September 30, 2004 (Table 3). The sensitivity of PRZM to Kd decreased with increasing rainfall intensity on May 2 (Table 3). PRZM outputs were much less sensitive to soil properties than Kd values but the sensitivity to changes in soil properties also decreased with increasing rainfall intensity (Table 3). When soil properties or Kd values in knoll profiles were replaced by those measured in toeslope profiles, Kd was again the most sensitive input parameter (Table 4). The sensitivity of PRZM to changes in soil properties or Kd values again decreased with increasing rainfall intensity on May 2 (Table 4).

There was an increased sensitivity to SOC when Koc was used in the simulations rather than Kd (Tables 3 and 4). In the Koc scenario,

Table 2
Estimates of the cumulative amount of 2,4-D leached in three soil profiles from its application date on May 1, 2004 to September 30, 2004. There were six simulated rainfall scenarios (R1 to R6). All numbers refer to scenario L1 (Table 1).

Rainfall on May 2[a]	Knoll			Toeslope			Trough		
	Leached		Water	Leached		Water	Leached		Water
(mm)	(g ha^{-1})	(%)[b]	(cm)	(g ha^{-1})	(%)	(cm)	(g ha^{-1})	(%)	(cm)
15 cm depth									
R1: 0[a]	26.62	5.98	23	0.09	0.02	21	0.13	0.03	21
R2: 28.4	43.41	9.75	25	0.22	0.05	23	0.27	0.06	23
R3: 51.6	79.60	17.88	27	1.07	0.24	25	1.29	0.29	25
R4: 86.9	140.33	31.52	31	8.73	1.96	28	9.75	2.19	28
R5: 141	208.00	46.72	36	37.35	8.39	34	39.89	8.96	34
R6: 384	319.25	71.71	61	169.27	38.02	58	173.41	38.95	58
45 cm depth									
R1: 0	0.13	0.03	16	0.00	0.00	13	0.00	0.00	13
R2: 28.4	0.31	0.07	18	0.00	0.00	15	0.00	0.00	15
R3: 51.6	2.00	0.45	20	0.00	0.00	18	0.00	0.00	17
R4: 86.9	14.51	3.26	24	0.00	0.00	21	0.00	0.00	21
R5: 141	52.49	11.79	29	0.13	0.03	27	0.13	0.03	26
R6: 384	193.48	43.46	53	20.92	4.70	51	21.41	4.81	51
60 cm depth									
R1: 0	0.00	0.00	14	0.00	0.00	11	0.00	0.00	10
R2: 28.4	0.04	0.01	16	0.00	0.00	13	0.00	0.00	12
R3: 51.6	0.40	0.09	18	0.00	0.00	15	0.00	0.00	15
R4: 86.9	5.65	1.27	22	0.00	0.00	18	0.00	0.00	18
R5: 141	30.05	6.75	27	0.00	0.00	24	0.00	0.00	24
R6: 384	158.45	35.59	51	8.46	1.90	48	9.88	2.22	48
100 cm depth									
R1: 0	–[c]	–	–	0.00	0.00	9	0.00	0.00	9
R2: 28.4	–	–	–	0.00	0.00	11	0.00	0.00	11
R3: 51.6	–	–	–	0.00	0.00	13	0.00	0.00	13
R4: 86.9	–	–	–	0.00	0.00	17	0.00	0.00	17
R5: 141	–	–	–	0.00	0.00	22	0.00	0.00	22
R6: 384	–	–	–	3.29	0.74	46	1.60	0.36	46
160 cm depth									
R1: 0	–	–	–	–	–	–	0.00	0.00	8
R2: 28.4	–	–	–	–	–	–	0.00	0.00	10
R3: 51.6	–	–	–	–	–	–	0.00	0.00	12
R4: 86.9	–	–	–	–	–	–	0.00	0.00	16
R5: 141	–	–	–	–	–	–	0.00	0.00	22
R6: 384	–	–	–	–	–	–	0.40	0.07	46

[a] Actual rainfall at Morris on May 2, 2004. Amount of rainfall from May 1 to September 30, 2004 was 515.8 mm in total (Fig. 2).
[b] As a percentage of the amount of 2,4-D applied (445.2 g ha^{-1}).
[c] not determined.

Table 3
Effect of replacing data on sorption or soil properties in the toeslope profile by data measured in the knoll profile on estimating the cumulative amount of 2,4-D leached to 15 cm depth from its application date on May 1, 2004 to September 30, 2004. There were six simulated rainfall scenarios (R1 to R6). Data are expressed as a % of that was leached to 15 cm depth in the toeslope profile under base scenario L1 (Table 2). This cumulative amount of 2,4-D leached under L1 was 0.09, 0.22, 1.07, 8.73, 37.35 and 169.27 g ha^{-1} for simulated rainfall scenarios 0, 28.4, 51.6, 86.9. 141 and 384 mm, respectively (Table 2). The amount of 2,4-D applied to soil was 445.2 g ha^{-1}.

Rainfall on May 2 (mm)	Simulations using Kd	Simulations using Koc
Leached as % of base scenario L1		
Replacing either Kd (left column) or Koc (right column)		
R1: 0[a]	29,081	1197
R2: 28.4	20,882	1066
R3: 51.6	8,009	684
R4: 86.9	1715	338
R5: 141	584	211
R6: 384	192	132
Replacing SOC		
R1: 0	117	12,866
R2: 28.4	116	9779
R3: 51.6	112	4231
R4: 86.9	106	1111
R5: 141	103	442
R6: 384	101	173
Replacing bulk density		
R1: 0	59	59
R2: 28.4	60	60
R3: 51.6	66	66
R4: 86.9	77	77
R5: 141	85	85
R6: 384	94	94
Replacing soil texture		
R1: 0	96	96
R2: 28.4	96	96
R3: 51.6	95	95
R4: 86.9	95	95
R5: 141	96	96
R6: 384	98	98
Replacing both SOC and Kd (left column) or SOC and Koc (right column)		
R1: 0	31,430	31,430
R2: 28.4	22,573	22,573
R3: 51.6	8499	8499
R4: 86.9	1780	1780
R5: 141	597	597
R6: 384	194	194
Replacing SOC, bulk density and soil texture		
R1: 0	84	10,987
R2: 28.4	84	8354
R3: 51.6	81	3595
R4: 86.9	81	976
R5: 141	86	405
R6: 384	94	167

[a] Actual rainfall at Morris on May 2, 2004. Amount of rainfall from May 1 to September 30, 2004 was 515.8 mm in total (Fig. 2).

Table 4
Effect of replacing data on sorption or soil properties in the knoll profile by data measured in the toeslope profile on estimating the cumulative amount of 2,4-D leached to 15 cm depth from its application date on May 1, 2004 to September 30, 2004. There were six simulated rainfall scenarios (R1 to R6). Data are expressed as a % of that was leached to 15 cm depth in the knoll profile under base scenario L1 (Table 2). This cumulative amount of 2,4-D leached under L1 was 26.62, 43.42, 79.60, 140.33, 208.00 and 319.25 g ha^{-1} for simulated rainfall scenarios 0, 28.4, 51.6, 86.9. 141 and 384 mm, respectively (Table 2). The amount of 2,4-D applied to soil was 445.2 g ha^{-1}.

Rainfall on May 2 (mm)	Simulations using Kd	Simulations using Koc
Leached as % of base scenario L1		
Replacing either Kd (left column) or Koc (right column)		
R1: 0[a]	3E-01	40
R2: 28.4	4E-01	42
R3: 51.6	1	48
R4: 86.9	5	61
R5: 141	15	73
R6: 384	50	89
Replacing SOC		
R1: 0	91	3
R2: 28.4	92	4
R3: 51.6	94	7
R4: 86.9	96	17
R5: 141	98	33
R6: 384	99	66
Replacing bulk density		
R1: 0	106	106
R2: 28.4	106	106
R3: 51.6	106	106
R4: 86.9	104	104
R5: 141	103	103
R6: 384	101	101
Replacing soil texture		
R1: 0	107	107
R2: 28.4	108	108
R3: 51.6	108	108
R4: 86.9	106	106
R5: 141	104	104
R6: 384	102	102
Replacing both SOC and Kd (left column) or SOC and Koc (right column)		
R1: 0	2E-01	2E-01
R2: 28.4	3E-01	3E-01
R3: 51.6	1	1
R4: 86.9	5	5
R5: 141	15	15
R6: 384	49	49
Replacing SOC, bulk density and soil texture		
R1: 0[1]	105	4
R2: 28.4	105	5
R3: 51.6	107	9
R4: 86.9	107	21
R5: 141	105	38
R6: 384	102	70

[a] Actual rainfall at Morris on May 2, 2004. Amount of rainfall from May 1 to September 30, 2004 was 515.8 mm in total (Fig. 2).

both SOC and Koc are used in PRZM to calculate Kd values. There were larger difference between knoll and footslope profiles in SOC (Fig. 3C) than Koc (Fig. 3J), and hence replacing SOC had a greater impact on the % leached than changing Koc (Tables 3 and 4).

When soil profile segments were assigned an average Kd value derived from the A-horizon (L3: Table 1), the amount of 2,4-D leached was lower than when profile segments were assigned an average value derived from the entire soil profile (L2: Table 1) (Tables 5–7). For example, reducing the average Kd values in the knoll profile by approximately two-fold, from 0.44 L kg^{-1} (L3) to 0.28 L kg^{-1} (L2), resulted in an approximately two-fold increase in 2,4-D leaching to 15 cm depth under the climatic conditions occurring at the site between May 1 and September 30, 2004 (R1) (Table 5). The sensitivity of PRZM to such changes in Kd values was even more pronounced for the toeslope (Table 6) and trough (Table 7) profiles. Specifically, under the actual climatic scenario R1, reducing the average Kd values in the toeslope profile by two-thirds, from 1.64 L kg^{-1} (L3) to 1.06 L kg^{-1} (L2), resulted in about 20 times more 2,4-D leaching to 15 cm depth (Table 6); and reducing the average Kd values in the trough by approximately two-fold, from 1.57 L kg^{-1} (L3) to 0.86 L kg^{-1} (L2), resulted in 36 times more 2,4-D leaching to 15 cm depth (Table 7). Therefore, relatively small changes to Kd resulted in relatively large differences in estimates of the amount of 2,4-D leached to 15 cm depth. The sensitivity of PRZM to these changes in Kd generally decreased with increasing rainfall intensity (Tables 5–7).

In the knoll profile, when soil profile segments were assigned an average Kd value derived from each horizon (L4: Table 1), the predicted amounts of 2,4-D leached to 15, 45 and 60 cm depth were relatively close to those predicted under the base scenario (L1) (Table 5). Relatively to the amount of 2,4-D leached under the base scenario (L1) in the knoll profile, the results for L4 were better than those for L2 and L3 (Table 5). L3 demonstrated particularly poor results for both deeper depths, 45 and 60 cm.

Regardless of the way in which Kd values were assigned to soil profile segments, the amounts of 2,4-D leached to 45 cm or deeper depths were very small in both the toeslope (Table 6) and trough (Table 7) profiles. For the amount of 2,4-D leached to 15 cm depth, the results of both L3 and L4 were similar to that predicted under the base scenario (L1) (Tables 6 and 7). Relatively to the amounts of 2,4-D leached under the base scenario (L1), the results for L2 were poor in both the toeslope (Table 6) and trough (Table 7) profiles.

Considering all soil samples, the 2,4-D Kd was significantly positively associated with SOC (Fig. 4A) and CEC (Fig. 4B), but negatively associated with clay (Fig. 4C). The association between soil pH and 2,4-D Kd was closest to a Gaussian distribution ($r=0.75$) where all soil samples from the alkaline knoll profile had Kd values below the average value of 1.03 L kg^{-1} (Fig. 4D), possibly because of their low

Table 5
Estimates of the cumulative amount of 2,4-D leached in the knoll profile from its application date on May 1, 2004 to September 30, 2004. There were six simulated rainfall scenarios (R1 to R6). L1 to L4 refer to the different ways by which PRZM layers were assigned Kd values (Table 1). The % leached refers to the cumulative amount of 2,4-D leached at 15 cm depth as a % of the amount of 2,4-D applied (445.2 g ha^{-1}). % L1 refers to the cumulative amount of 2,4-D leached at 15 cm depth as a % of the amount leached in the knoll profile under base scenario L1.

Rainfall on May 2 (mm)	Measured (L1)		$\overline{x}$ Soil profile (L2)		$\overline{x}$ A-horizon (L3)		$\overline{x}$ Soil horizon (L4)	
	Leached (%)	% L1	Leached (%)	% L1	Leached (%)	% L1	Leached (%)	% L1
15 cm depth								
R1: 0[a]	5.98	100	11.53	193	5.89	98	5.89	98
R2: 28.4	9.75	100	18.43	189	9.62	99	9.62	99
R3: 51.6	17.88	100	30.43	170	17.68	99	17.68	99
R4: 86.9	31.52	100	45.34	144	31.26	99	31.26	99
R5: 141	46.72	100	59.07	126	46.48	99	46.48	99
R6: 384	71.71	100	78.41	109	71.55	100	71.55	100
45 cm depth								
R1: 0	0.03	100	0.06	200	0.00	[0][b]	0.03	100
R2: 28.4	0.07	100	0.14	200	0.01	14	0.08	114
R3: 51.6	0.45	100	0.75	167	0.07	16	0.50	111
R4: 86.9	3.26	100	4.45	137	1.08	33	3.46	106
R5: 141	11.79	100	14.22	121	6.04	51	12.19	103
R6: 384	43.46	100	46.54	107	34.05	78	43.98	101
60 cm depth								
R1: 0	0.00	100	0.00	–[c]	0.00	–	0.00	–
R2: 28.4	0.01	100	0.01	100	0.00	[0]	0.01	100
R3: 51.6	0.09	100	0.08	89	0.00	[0]	0.09	100
R4: 86.9	1.27	100	1.20	94	0.18	14	1.26	99
R5: 141	6.75	100	6.52	97	2.05	30	6.70	99
R6: 384	35.59	100	35.14	99	23.05	65	35.45	100

[a] Actual rainfall at Morris on May 2, 2004. Amount of rainfall from May 1 to September 30, 2004 was 515.8 mm in total (Fig. 2).
[b] Unable to calculate because there was no leaching under this simulated scenario.
[c] No leaching under L1 and no leaching under the simulated scenario.

Table 6
Estimates of the cumulative amount of 2,4-D leached in the toeslope profile from its application date on May 1, 2004 to September 30, 2004. There were six simulated rainfall scenarios (R1 to R6). L1 to L4 refer to the different ways by which PRZM layers were assigned Kd values (Table 1). The % leached refers to the cumulative amount of 2,4-D leached at 15 cm depth as a % of the amount of 2,4-D applied (445.2 g ha^{-1}). % L1 refers to the cumulative amount of 2,4-D leached at 15 cm depth as a % of the amount leached in the toeslope profile under base scenario L1.

Rainfall on May 2 (mm)[a]	Measured (L1)		$\bar{x}$ Soil profile (L2)		$\bar{x}$ A-horizon (L3)		$\bar{x}$ Soil horizon (L4)	
	Leached (%)	% L1	Leached (%)	% L1	Leached (%)	% L1	Leached (%)	% L1
15 cm depth								
R1: 0[a]	0.02	100	0.39	1,950	0.02	100	0.02	100
R2: 28.4	0.05	100	0.78	1560	0.04	80	0.04	80
R3: 51.6	0.24	100	2.26	942	0.22	92	0.22	92
R4: 86.9	1.96	100	8.12	414	1.90	97	1.90	97
R5: 141	8.39	100	20.08	239	8.27	99	8.27	99
R6: 384	38.02	100	52.46	138	37.87	100	37.87	100
45 cm depth								
R1: 0[a]	0.00	100	0.00	–[b]	0.00	–	0.00	–
R2: 28.4	0.00	100	0.00	–	0.00	–	0.00	–
R3: 51.6	0.00	100	0.00	–	0.00	–	0.00	–
R4: 86.9	0.00	100	0.01	–	0.00	–	0.00	–
R5: 141	0.03	100	0.34	1,133	0.02	67	0.07	233
R6: 384	4.70	100	11.93	254	4.24	90	6.65	141
60 cm depth								
R1: 0[a]	0.00	100	0.00	–	0.00	–	0.00	–
R2: 28.4	0.00	100	0.00	–	0.00	–	0.00	–
R3: 51.6	0.00	100	0.00	–	0.00	–	0.00	–
R4: 86.9	0.00	100	0.00	–	0.00	–	0.00	–
R5: 141	0.00	100	0.04	[0.18][c]	0.00	–	0.01	[0.04]
R6: 384	1.90	100	5.54	292	1.37	72	3.14	165
100 cm depth								
R1: 0[a]	0.00	100	0.00	–	0.00	–	0.00	–
R2: 28.4	0.00	100	0.00	–	0.00	–	0.00	–
R3: 51.6	0.00	100	0.00	–	0.00	–	0.00	–
R4: 86.9	0.00	100	0.00	–	0.00	–	0.00	–
R5: 141	0.00	100	0.00	–	0.00	–	0.00	–
R6: 384	0.74	100	0.62	84	0.05	7	0.71	96

[a] Actual rainfall at Morris on May 2, 2004. Amount of rainfall from May 1 to September 30, 2004 was 515.8 mm in total (Fig. 2).
[b] Unable to calculate because there was no leaching under this simulated scenario.
[c] No leaching under L1 so the amount of leached under the simulated scenario is given as g ha^{-1}.

SOC (<0.6%) (Fig. 3C). The soil pH was relatively constant in toeslopes (Fig. 3A) but samples below 64 cm depth had SOC values <0.5% (Fig. 3C) and demonstrated 2,4-D Kd values <1.03 L kg^{-1} (Fig. 4D), while samples from 0–64 cm depth had SOC values >0.7% (Fig. 3C) and 2,4-D Kd values >1.03 L kg^{-1} (Fig. 4D). Similarly, although surface soils in the trough profile were relatively alkaline (Fig. 3A) their SOC was typically >0.8% (Fig. 3C), therefore demonstrated 2,4-D Kd values >1.03 L kg^{-1} (Fig. 4D). In contrast, the more acidic samples from deeper depths in the trough profile (Fig. 3A) typically contained SOC <0.8% (Fig. 3C) and exhibited 2,4-D Kd values <1.03 L kg^{-1} (Fig. 4D).

There was no clear trend in the association between SOC and 2,4-D Koc (Fig. 5A). The 2,4-D Koc was below average for most samples in the alkaline knoll profile (Fig. 5A), while the 2,4-D Koc values in the trough profile were particularly large at depths between 150 and 160 cm (Fig. 3J) where the pH is relatively acidic (Fig. 3A). Consequently, considering all soil samples, there was a negative association between soil pH and 2,4-D Koc (Fig. 5B). The 2,4-D Koc was not significantly associated with clay content and CEC (data not shown).

Considering all soil samples, there was no clear trend in the association between 2,4-D Kd and glyphosate Kd or between 2,4-D Koc and glyphosate Koc (data not shown). Considering each individual soil profile, there was a positive linear association between 2,4-D Kd and glyphosate Kd in the knoll profile ($r=0.94$), a negative linear association in the trough ($r=0.69$), but no significant association in the toeslope profile. Considering each individual soil profile, there was no significant association between 2,4-D Koc and glyphosate Koc.

In all three soil profiles, the associations between SOC and either glyphosate Kd (Fig. 6A) or glyhosate Koc (Fig. 6B) were bimodal. Considering all soil samples, both glyphosate Kd (Fig. 6C) and Koc (Fig. 6D) were negatively associated with soil pH. Although surface samples in the trough profile contained more SOC (Fig. 3C), they were more alkaline (Fig. 3A) than subsurface samples and therefore had smaller glyphosate Kd (Figs. 3G and 6A) and Koc (Figs. 3H and 6B) values. Glyphosate Kd was positively associated with clay content (Fig. 6E), but there was no significant association between clay content and glyphosate Koc (data not shown). The soil pH was relatively constant with depth in the toeslope (Fig. 3A) and, although

Table 7
Estimates of the cumulative amount of 2.4-D leached in the trough profile from its application date on May 1, 2004 to September 30, 2004. There were six simulated rainfall scenarios (R1 to R6). L1 to L4 refer to the different ways by which PRZM layers were assigned Kd values (Table 1). The % leached refers to the cumulative amount of 2,4–D leached at 15 cm depth as a % of the amount of 2,4-D applied (445.2 g/ha). % L1 refers to the cumulative amount of 2,4-D leached at 15 cm depth as a % of the amount leached in the trough profile under base scenario L1.

Rainfall on May 2 (mm)	Measured (L1)		$\bar{x}$ Soil profile (L2)		$\bar{x}$ A-horizon (L3)		$\bar{x}$ Soil horizon (L4)	
	Leached (%)	% L1	Leached (%)	% L1	Leached (%)	% L1	Leached (%)	% L1
15 cm depth								
R1: 0[a]	0.03	100	1.08	3,600	0.03	100	0.03	100
R2: 28.4	0.06	100	2.00	3,333	0.07	117	0.07	117
R3: 51.6	0.29	100	4.81	1,659	0.31	107	0.31	107
R4: 86.9	2.19	100	13.09	598	2.27	104	2.27	104
R5: 141	8.96	100	26.87	300	9.14	102	9.14	102
R6: 384	38.95	100	58.32	150	39.18	101	39.18	101
45 cm depth								
R1: 0	0.00	100	0.00	–[b]	0.00	–	0.00	–
R2: 28.4	0.00	100	0.00	–	0.00	–	0.00	–
R3: 51.6	0.00	100	0.00	–	0.00	–	0.00	–
R4: 86.9	0.00	100	0.04	[0.18][c]	0.00	–	0.00	–
R5: 141	0.03	100	0.85	2,833	0.03	100	0.03	100
R6: 384	4.81	100	16.69	347	4.68	97	4.93	102
60 cm depth								
R1: 0	0.00	100	0.00	–	0.00	–	0.00	–
R2: 28.4	0.00	100	0.00	–	0.00	–	0.00	–
R3: 51.6	0.00	100	0.00	–	0.00	–	0.00	–
R4: 86.9	0.00	100	0.00	–	0.00	–	0.00	–
R5: 141	0.00	100	0.14	[0.62]	0.00	–	0.01	[0.04]
R6: 384	2.22	100	8.67	391	1.55	70	2.86	129
100 cm depth								
R1: 0	0.00	100	0.00	–	0.00	–	0.00	–
R2: 28.4	0.00	100	0.00	–	0.00	–	0.00	–
R3: 51.6	0.00	100	0.00	–	0.00	–	0.00	–
R4: 86.9	0.00	100	0.00	–	0.00	–	0.00	–
R5: 141	0.00	100	0.00	–	0.00	–	0.00	–
R6: 384	0.36	100	1.32	367	0.06	17	0.66	183
160 cm depth								
R1: 0	0.00	100	0.00	–	0.00	–	0.00	–
R2: 28.4	0.00	100	0.00	–	0.00	–	0.00	–
R3: 51.6	0.00	100	0.00	–	0.00	–	0.00	–
R4: 86.9	0.00	100	0.00	–	0.00	–	0.00	–
R5: 141	0.00	100	0.00	–	0.00	–	0.00	–
R6: 384	0.09	100	0.07	78	0.00	[0]	0.09	100

[a] Actual rainfall at Morris on May 2, 2004. Amount of rainfall from May 1 to September 30, 2004 was 515.8 mm in total (Fig. 2).
[b] Unable to calculate because there was no leaching under this simulated scenario.
[c] No leaching under L1 so the amount of leached under the simulated scenario is given as g/ha.

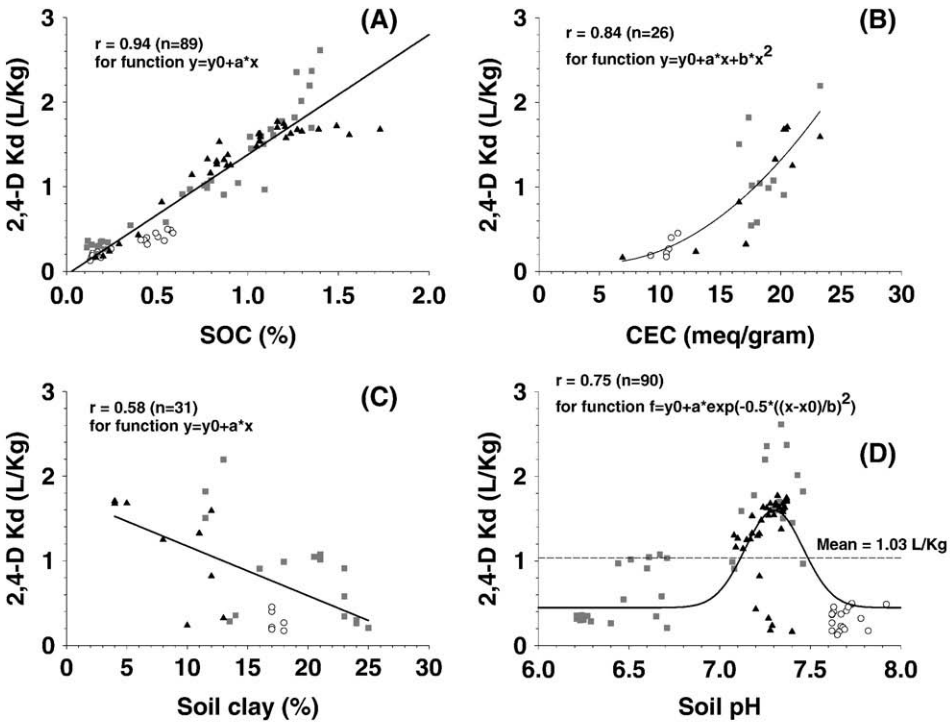

Fig. 4. Associations between the 2,4-D sorption coefficient and one of the following parameters (A) soil organic carbon content, (B) cation exchange capacity, (C), clay content, and (D) soil pH for data obtained in soil profiles of knoll (eroded-upper slope) (white circles), trough (eroded water-way) (grey squares), and toeslope (deposition zone) (black triangles) landform elements.

surface samples in the toeslope profile contained more SOC (Fig. 3C), they had typically a less clay content (Fig. 3E) than subsurface samples and therefore had smaller glyphosate Kd values (Figs. 3G and 6A). In the knoll profile, both soil pH (Fig. 3A) and clay content (Fig. 3E) were relatively constant, but surface soils with slightly greater SOC demonstrated greater glyphosate Kd values, relative to subsurface soils (Fig. 6A). There were no significant associations between CEC and either glyphosate Kd or Koc (data not shown).

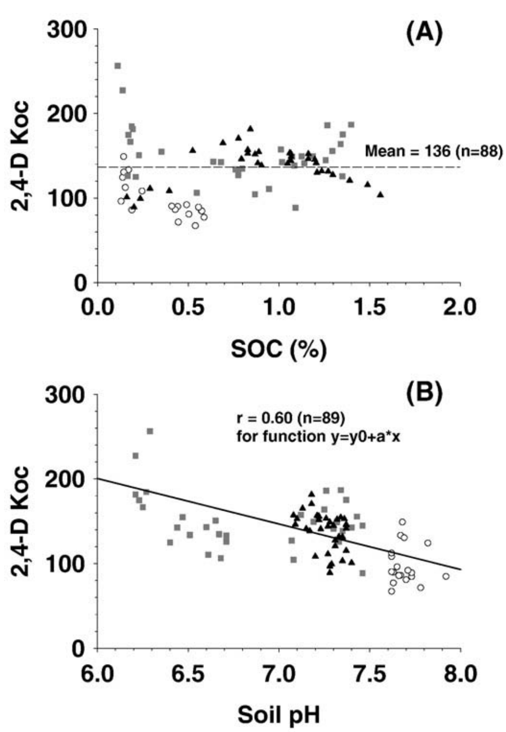

Fig. 5. Associations between the 2,4-D sorption per unit soil organic carbon and either (A) soil pH or (B) soil organic carbon content, for data obtained in soil profiles of knoll (eroded-upper slope) (white circles), trough (eroded water-way) (grey squares), and toeslope (deposition zone) (black triangles) landform elements.

4. Discussion

Considering all soil samples, glyphosate sorption was negatively related with soil pH and positively associated with clay content. The relation between SOC and glyphosate Kd was less clear, even though Piccolo et al. (1996) concluded that glyphosate is more strongly sorbed by humic extracts from soil than clay minerals. Most subsurface soil samples in the trough profile demonstrated large glyphosate Kd values despite their very low SOC; and these subsurface samples were relatively acidic and had large clay contents. It is long known that glyphosate is readily bound to clay minerals and that its sorption by such soil constituents increases with decreasing soil pH because glyphosate acid has pKa values of 2.5, 5.6 and 10.3 (Sprankle et al., 1975; McConnel and Hossner, 1985; Vencill, 2002). Gimsing et al. (2004) found that soil pH was the only influencing factor on glyphosate sorption by surface soils, even though soil properties such as SOC and clay content and mineralogy were also measured.

There was a positive linear relation between SOC and 2,4-D Kd, as observed for other surface and subsurface soils in agricultural fields (Farenhorst et al., 2003; Gaultier et al., 2006; Farenhorst et al., 2008). This is not surprising because soil organic carbon content is the primary factor influencing 2,4-D sorption (Reddy and Gambrell, 1987; Mallawatantri and Mulla, 1992; Hermosin and Cornejo, 1993; Johnson et al., 1995). In agreement with other studies (Hermosin and Cornejo, 1991), we also observed a negative linear relation between clay content and 2,4-D Kd. However, soil clay content had no significant influence on the sorption of 2,4-D in soil horizons of a conventional-tilled soil-landscape in Canada (Gaultier et al., 2006).

Experimental field studies have been conducted to test the accuracy of pesticide fate models such as PRZM which provides for a

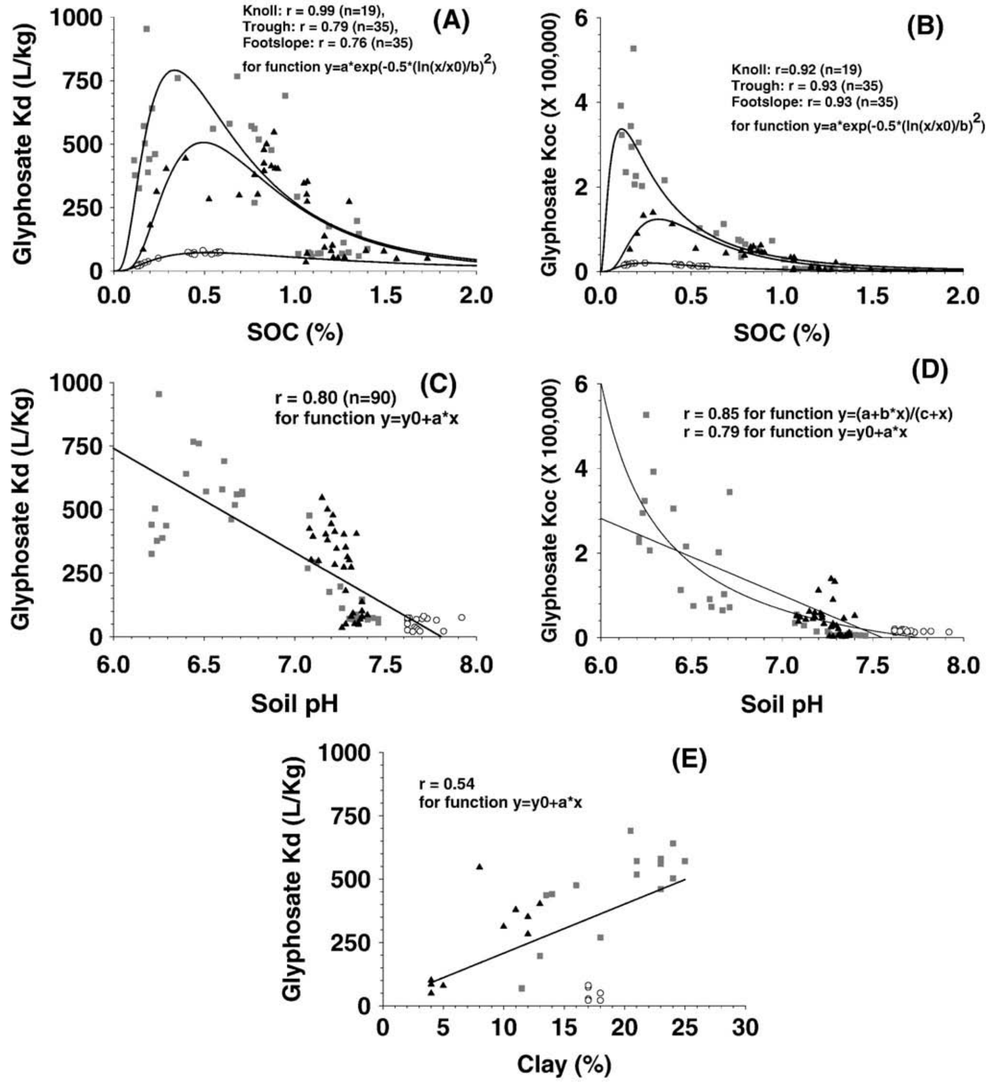

Fig. 6. Associations between the glyphosate sorption coefficient and one of the following parameters (A) soil organic carbon content, (C) soil pH and (E) soil clay content, as well as the associations between the glyphosate sorption per unit soil organic carbon and either (B) soil organic carbon content or (D) soil pH, for data obtained in soil profiles of knoll (eroded-upper slope) (white circles), trough (eroded water-way) (grey squares), and toeslope (deposition zone) (black triangles) landform elements.

reasonable estimate of processes operating on a pesticide (Nicholls, 1994; Sadeghi et al., 1995; Carsel et al., 1998; Malone et al., 1999). Our study demonstrates that PRZM output is more sensitive to the pesticide input parameter, Kd, than to soil properties input data. Dann et al. (2006) applied three other pesticide fate models to a field-site near Hamilton, New Zealand, and also concluded that site-specific data on the pesticide sorption parameter were more important than the quality of the soil properties information used. In fact, site-specific data on pesticide sorption and half-lives are possibly more important to the success of regulatory assessments than the choice of the pesticide fate model itself (Dann et al., 2006).

In our study, landform elements such as eroded knolls demonstrated distinct lesser Kd values in the soil profile relative to soil profiles in other landform elements such as the trough and toeslopes. The spatial variability of Kd in a field, as influenced by land management practices, should be further studied as we demonstrate here that such variations will influence the outcome of model simulations. Given that the field has been moldboard plowed on an annual basis for at least 40 years, soil redistribution by tillage has had an impact on soil profile characteristics (Lindstrom et al., 1992; Li et al., 2007; Papiernik et al., 2007). Relative to concave elements, the eroded knoll profile is particularly low in SOC and therefore the 2,4-D Kd is relatively small throughout the eroded knoll profile. Soil profiles in concave elements will become progressively buried with topsoil from convex elements (De Alba et al., 2004). With further degradation of the convex elements by tillage-erosion, we expect that surface soils in concave elements will also become progressively lower in SOC. Because SOC controls 2,4-D sorption by soil, soil-landscape degradation by tillage erosion would ultimately result in an overall lesser retention of 2,4-D by surface soils across the entire field. We demonstrate that such soil-landscape degradation could have implications for 2,4-D leaching to depth because — in an extreme scenario of replacing the Kd values of toeslope profiles (ranging from 0.16 to 1.77 L kg^{-1}) by those measured in knoll profiles (ranging from 0.12 to 0.50 L kg^{-1}) — the amount of herbicide leached to a 15 cm depth increased by 29,081% under an actual rainfall scenario.

The intensity of collecting Kd data across landform elements but also with depth is off-course limited by the level of financial resources. In all soil profiles, relative to the results of the base case (L1), assigning Kd values based on surface soil (L3) generally underestimated the amount of 2,4-D leached to subsurface soils. Assigning Kd values based on soil horizons (L4) generally resulted in estimates closer to the base scenario results (L1). These results suggest that risk assessments of herbicide leaching to depth require data on herbicide sorption throughout the entire soil profile. However, herbicide sorption processes are more frequently studied in surface soils than subsurface soils (Gaultier et al., 2006).

In regional-scale assessments of the risk of pesticide off-site movement, data on soil properties are usually derived from generic databases describing the characteristics of horizons within soil series (e.g., McQueen et al., 2007). Data on Kd values are typically not available, therefore users of pesticide fate models utilize a single Koc value (e.g., Wilson et al., 1996, McQueen et al., 2007). Although this is a logical choice — because Koc reflects the sorption of a pesticide per unit soil organic carbon and is a universal approach for normalizing pesticide sorption across a range of soil types (Wauchope et al., 2002) — the Koc values in this study varied with landform elements and to depth. When using Koc in the simulations, PRZM was relatively sensitive to changes in either Koc or SOC because of the influence of these input parameters on calculating Kd values. As such, in addition to accurate SOC data for horizons within soil series, a better estimate of how Koc values vary among soil horizons (Gaultier et al., 2006) is important to reduce the error associated with current regional-scale assessments in policy analyses.

We observed some differences in 2,4-D Koc values that could not be readily explained by variations in the values of soil properties such as SOC, soil pH, carbonate content, CEC and soil texture. Thus, perhaps additional studies on the influence of soil organic matter characteristics on herbicide sorption in soil profiles are particularly important (Ding et al., 2002; Farenhorst, 2006).

This study assumed that all landform elements received the same amount of water, all in the form of rain. Our results are therefore limited in that, under field conditions, the toeslope, but particularly the trough where water converges, would have received additional water inputs. Revising one-dimensional models such as PRZM by including the distribution of water flow in strongly-eroded landscapes, may further improve the usefulness of this model in policy analyses at large scales.

5. Conclusion

Distinct herbicide sorption coefficients were found for soil profiles from three landform elements in a heavily-tilled calcareous prairie landscape. The 2,4-D Kd varied with depth in all three landform elements from 0.12 to 0.50 L kg^{-1} in the knoll, from 0.21 to 2.61 L kg^{-1} in the trough and from 0.16 to 1.77 L kg^{-1} in the toeslope. Regardless of the landform element and depth, soil samples with SOC<0.8% always exhibited 2,4-D Kd values<1.03 L kg^{-1}. The sensitivity of PRZM simulations to small changes to Kd was demonstrated by inserting Kd data from the knoll profile into the toeslope profile which resulted in 29,081% more estimated leaching to 15 cm depth in the toeslope profile under the climatic conditions at the site. Relative to using measured Kd values obtained from 2-cm profile segments, assigning an average Kd by soil horizon yielded better results than assigning a single average Kd value to the entire soil profile. Consequently, studies on a wider range of soil-landscapes are required to improve on functions to estimate 2,4-D Kd values by depth and landscape position as the availability of such functions could strengthen pesticide fate simulations at large-scales. PRZM was not very sensitive to inputs of soil properties, expect in cases when Koc and SOC were used in calculating Kd values. Glyphosate sorption by soil was more controlled by soil pH and clay content than SOC, with glyphosate Kd values ranging from 19 to 80 L kg^{-1} in the knoll, 56 and 954 L kg^{-1} in the trough and from 35 to 547 L kg^{-1} in the toeslope. The strong sorption of glyphosate by soil resulted in this herbicide being immobile in all landform elements even under the largest 24-h rainfall event (384 mm) ever recorded for a location in MN.

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References

Boesten, J.J.T.I., van der Linden, A.M.A., 1991. Modeling the influence of sorption and transformation on pesticide leaching and persistence. J. Environ. Qual. 20, 425–435.
Calvet, R., 1989. Adsorption of organic chemicals in soils. Environ. Health Persp. 83, 145–177.
Carsel, R.F., Imhoff, J.C., Hummel, P.R., Cheplick, J.M. and Donigan, A.S.J. 1998. PRZM-3. A model for predicting pesticide and nitrogen fate in the crop root and unsaturated soil zones: user manual for release 3.0, National Exposure Research Laboratory, Office of Research and development, U.S. Environmental Protection Agency, Athens, Georgia, U.S.A. [Online WWW]. Available URL " http://www.epa.gov/ ceampubl/gwater/przm3/index.htm" [Accessed August 2003].
Chapman, H.D., 1965. Cation-exchange capacity. In: Black, C.A. (Ed.), Methods of soil analysis. Part 2. Chemical and microbiologial properties. ASA, SSSA, Madison, WI, pp. 891–901.
Climatology Working Group, 2007. Rainfall totals for southern Minnesota August 18 through August 20 (8:00 AM CDT), 2007. [Online WWW]. Available URL "http://climate.umn.edu/doc/journal/flash_floods/ff070820.htm" [Accessed November 2007].
Dann, R.L., Close, M.E., Lee, R., Pang, L., 2006. Impact of data quality and model complexity on prediction of pesticide leaching. J. Environ. Qual. 35, 628–640.
De Alba, S., Lindstrom, M., Schumacher, T.E., Malo, D.D., 2004. Soil landscape evolution due to soil redistribution by tillage: a new conceptual model of soil catena evolution in agricultural landscapes. Catena 58, 77–100.
De Jonge, H., De Jonge, L.W., Jacobsen, O.H., Yamaguchi, T., Moldrup, P., 2001. Glyphosate sorption in soils of different pH and phosphorus content. Soil Sci. 166, 230–238.
Ding, G., Novak, J.M., Herbert, S., Xing, B., 2002. Long-term tillage effects on soil metolachlor sorption and desorption behavior. Chemosphere 48, 897–904.
Dubus, I.G., Brown, C.D., Beulke, S., 2003. Sensitivity analyses for four pesticide leaching models. Pest Manag. Sci. 59, 962–982.
Farenhorst, A., 2006. Importance of soil organic matter fractions in soil-landscape and regional assessments of pesticide sorption and leaching in soil. Soil Sci. Soc. Am. J. 70, 1005–1012.
Farenhorst, A., Florinski, I., Monreal, C., Muc, D., 2003. Evaluating the use of digital terrain modeling for quantifying the spatial variability of 2,4-D sorption within agricultural landscapes. Can. J. Soil Sci. 83, 557–564.
Farenhorst, A., Papiernik, S.K., Saiyed, I., Messing, P., Stephens, K.D., Schumacher, J.A., Lobb, D.A., Li, S., Lindstrom, M.J., Schumacher, T.E., 2008. Herbicide sorption coefficients in relations to soil properties and terrain attributes on a cultivated prairie. J. Environ. Qual. 37, 1201–1208.
FOOTPRINT Consortium, 2006. FOOTPRINT creating tools for pesticide risk assessment and management in Europe [Online WWW]. Available URL "http://www.eu-footprint.org/home.html." [Accessed November 2007].
Gaultier, J., Farenhorst, A., Crow, G., 2006. Spatial variability of soil properties and 2,4-D sorption in a hummocky field as affected by landscape position and soil depth. Can. J. Soil Sci. 86, 89–95.
Gee, G.W., Bauder, J.W., 1986. Particle-size analysis. In: Klute, A. (Ed.), Methods of soil analysis. Part 1. Physical and mineralogical methods. ASA, SSSA, Madison, WI, pp. 383–412.
Gimsing, A.L., Borggaard, O.K., Bang, M., 2004. Influence of soil composition on adsorption of glyphosate and phosphate by contrasting Danish surface soils. Euro. J. Soil Sci., 55, 183–191.
Hargreaves, G.H., Samani, J.W., 1985. Reference crop evapotranspiration from temperature. Appl. Eng. Agric. 1, 96–99.
Hermosin, M.C., Cornejo, J., 1991. Soil adsorption of 2,4-D as affected by the clay mineralogy. Toxicol. Environ. Chem. 31/32, 67–77.
Hermosin, M.C., Cornejo, J., 1993. Binding mechanism of 2,4-dichlorophenoxyacetic acid by organo-clays. J. Environ. Qual. 22, 325–331.
Huff, F.A. and Angel, J.R. 1992. Rainfall frequency atlas of the Midwest. Bulletin 71 (MCC Research report 92–03) Midwestern Climate Center and Illinois State Water Survey.
Jarvis, N. and Larsson, M. 1998. The MACRO model (version 4.3). Technical description, Swedish University of Agricultural Sciences (SLU), Department of Soil Sciences, Uppsala, Sweden. [Online WWW]. Available URL "http://www.mv.slu.se/BGF/MACROHTM/MACRO.HTM" [Accessed June 2005].
Johnson, W.G., Lavy, T.L., Gbur, E.E., 1995. Sorption, mobility, and degradation of triclopyr and 2,4-D in four soils. Weed Sci. 43, 678–684.
Li, S., Lobb, D.A., Lindstrom, M.J., Farenhorst, A., 2007. Tillage and water erosion in cultivated fields of the northern North American Great Plains evaluated using ^{137}Cs measurements and soil erosion models. Catena 70, 493–505.
Li, S., Lobb, D.A., Lindstrom, M.J., Papiernik, K., Farenhorst, A., 2008. Modeling tillage-induced redistribution of soil mass and its constituents within different landscapes. Soil Sci. Soc. Am. J. 72, 167–179.
Lindstrom, M.J., Nelson, W.W., Schumacher, T.E., 1992. Quantifying tillage erosion rates due to moldboard plowing. Soil Tillage Res. 24, 243–255.
Loeppert, R.H., Suarez, D.L., 1996. Carbonate and gypsum. In: Bartels, J.M. (Ed.), Methods of soil analysis. Part 3. Chemical methods. ASA, SSSA, Madison, WI, pp. 437–475.
Mallawatantri, A.P., Mulla, D.J., 1992. Herbicide adsorption and organic carbon contents on adjacent low-input versus conventional farms. J. Environ. Qual. 21, 546–551.
Malone, R.W., Warner, R.C., Workman, S.R., Byers, M.E., 1999. Modeling surface and subsurface pesticide transport under three field conditions using PRZM-3 and GLEAMS. Trans. ASAE 42, 1275–1288.

McConnel, J.S., Hossner, L.R., 1985. pH-Dependent adsorption isotherms of glyphosate. J. Agric. Food Chem. 33, 1075–1078.
McKeague, J.A., 1978. Manual on soil sampling and methods of analysis. Canadian Society of Soil Science, Ottawa, Canada.
McQueen, D.A.R., Farenhorst, A., Allaire, S., Cessna, A.J., 2007. Automation and evaluation of three pesticide fate models for a national analysis of leaching risk in Canada. Can. J. Soil Sci. 87, 203–212.
National Climatic Data Center, 2007. Archive weather data for a Morris, Minnesota site, 1999–2004. National Climatic Data Center, the Department of Commerce, National Oceanic and Atmospheric Administration and the National Environmental Satellite, Data and Information Service. [Online WWW]. Available URL "http://lwf.ncdc.noaa.gov/oa/climate/stationlocator.html" [Accessed November 2007].
Nelson, D.E., Sommers, L.E., 1982. Total carbon, organic carbon, and organic matter. In: Page, A.L. (Ed.), Methods of soil analysis. Part 2. Chemical and microbiological properties. ASA, SSSA, Madison, WI, pp. 539–577.
Nicholls, P.H., 1994. Simulation of the movement of bentazone in soils using the CALF and PRZM models. J. Environ. Sci. Health, Part A 29, 1157–1166.
Papiernik, S.K., Lindstrom, M.J., Schumacher, T.E., Schumacher, J.A., Malo, D.D., Lobb, D.A., 2007. Characterization of soil profiles in a landscape affected by long-term tillage. Soil Tillage Res. 93, 335–345.
Piccolo, A., Celano, G., Conte, P., 1996. Adsorption of glyphosate by humic substances. J. Agric. Food Chem. 44, 2442–2446.
Reddy, K., Gambrell, R., 1987. Factors affecting the adsorption of 2,4-D and methyl parathion in soils and sediments. Agric. Ecosyt. Environ. 18, 231–241.
Sadeghi, A.M., Isensee, A.R., Shirmohammadi, A., 1995. Atrazine movement in soil: comparison of field observations and PRZM simulations. J. Soil Contam. 4, 151–161.
Senesi, N., 1992. Binding mechanisms of pesticides to soil humic substances. Sci. Total Environ. 123/124, 63–76.
Soil Survey Staff 2008. Natural Resources Conservation Service, United States Department of Agriculture. Official Soil Series Descriptions [Online WWW]. Available URL: "http://soils.usda.gov/technical/classification/osd/index.html" [Accessed December 2008].
Sprankle, P., Meggitt, W.F., Penner, D., 1975. Adsorption, mobility, and microbial degradation of glyphosate in the soil. Weed Sci. 23, 229–234.
Symko, J., Farenhorst, A., 2008. 2,4-D mineralization in unsaturated and near-saturated surface soils of an undulating, cultivated, Canadian prairie landscape. J. Environ. Sci. Health, Part B. 43, 34–43.
Vencill, W.K. (Ed.), 2002. Herbicide handbook. Weed Science Society of America, Lawrence, KS, USA.
Wauchope, R.D., Yeh, S., Linders, B.H.J., Kloskowski, R., Tanaka, K., Rubin, B., Katayama, A., Kördel, W., Gerstl, Z., Lane, M., Unsworth, J.B., 2002. Pesticide soil sorption parameters: theory, measurement, uses, limitations, and reliability. Pest Manag. Sci. 58, 419–445.
Wilson, J.P., Inskeep, W.P., Wraith, J.M., Snyder, R.D., 1996. GIS-based solute transport modeling applications: scale effects of soil and climate data input. J. Environ. Qual. 25, 445–453.